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# Time-of-Flight Secondary Ion Mass Spectrometry of Deuterated Linear Poly(dimethylsiloxane)

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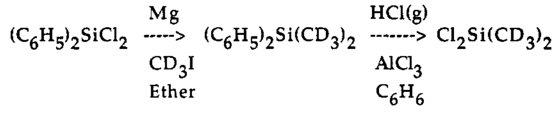
**Introduction.** Although deuterium labeling is very useful in assigning mass spectra, little has been published on the fully or selectively isotopically substituted polysiloxanes. A comparison of the ammonia chemical ionization (CI) mass spectra of the cyclic tetramers $\underline{[(CH_3)_2SiO]_4}$ and $\underline{[(CD_3)_2SiO]_4}$ has been reported.[1] Mass spectrometry (MS) however has previously proved to be very valuable for characterizing the thermal decomposition of poly(dimethylsiloxane) (PDMS) via pyrolysis-MS.[2] Secondary ion mass spectrometry (SIMS) has also been applied to identify the various fragments characteristic of PDMS[3-5] and thus give "fingerprint" spectra for identification purposes. More recently time-of-flight secondary ion mass spectrometry (TOFSIMS) has been used to show molar mass distributions in PDMS samples of molar mass <10 000 g mol$^{-1}$ [6] and to give information on polymerization reaction mechanisms by quantification of end-group functionalization/initiator incorporation.[7]

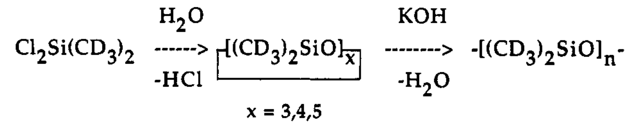
This paper describes the characterization of deuterated linear PDMS $-[(CD_3)_2SiO]_n-$ using time-of-flight secondary ion mass spectrometry. The work is part of a program investigating the conformations and interactions of deuterated siloxanes in isotopic blends $-[(CD_3)_2SiO]_n-/-[(CH_3)_2SiO]_n-$ using small-angle neutron scattering. It is therefore clearly important to demonstrate that no deuterium/hydrogen exchanges occurred during the synthetic methodology used.

**Experimental Section. Deuterated Poly(dimethylsiloxane) $-[(CD_3)_2SiO]_n-$ Synthesis.** The dichlorosilane $Cl_2Si(CD_3)_2$ precursor was synthesized using methods similar to those reported previously by Beltzung and co-workers,[8] the full details of which will be described elsewhere.[9] The $CD_3I$ was purchased from Cambridge Isotopes and incorporated using the scheme



$$(C_6H_5)_2SiCl_2 \xrightarrow[\substack{CD_3I\\ Ether}]{Mg} (C_6H_5)_2Si(CD_3)_2 \xrightarrow[\substack{AlCl_3\\ C_6H_6}]{HCl(g)} Cl_2Si(CD_3)_2$$

The dichlorosilane $Cl_2Si(CD_3)_2$ was then hydrolyzed, and the hydroxyl-terminated deuterated PDMS was obtained by ring-opening polymerization of the mixture of cyclic siloxanes $\underline{[(CD_3)_2SiO]_x}$ as shown below. The reaction was terminated using acetic acid, thus giving linear hydroxyl-terminated deuterated siloxane $HO[(CD_3)_2SiO]_nH$. A number-average molar mass $M_n$ of 7590 g mol$^{-1}$ and polydispersity index $M_w/M_n$ of 1.65 were obtained for the sample described here using a Waters gel permeation chromatograph, which was calibrated using PDMS standards.



$$Cl_2Si(CD_3)_2 \xrightarrow[-HCl]{H_2O} \underset{x\,=\,3,4,5}{\underline{[(CD_3)_2SiO]_x}} \xrightarrow[-H_2O]{KOH} -[(CD_3)_2SiO]_n-$$

**TOFSIMS Analysis.** TOFSIMS analyses were performed on a Kratos PRISM instrument. It was equipped with a reflectron-type time-of-flight mass analyzer and a 25-kV liquid metal ion source of monoisotopic $^{69}Ga^+$ ions with a minimum beam size of 500 Å. Positive and negative spectra were obtained at a pulse width of 10-50 ns, and a total integrated ion dose of about $10^{11}$ ions/cm$^2$. The mass resolution at 50 amu varied from $M/\Delta M$ = 1000 at 50-ns pulse width to about 2500 at 10-ns pulse width. For the time-of-flight secondary ion mass spectrometry (TOFSIMS) the homopolymer was dissolved in cyclohexane (2 wt %) and the sample coated onto a glass or stainless steel substrate at room temperature. After exhaustive solvent removal, the sample was then analyzed using TOFSIMS as described below.

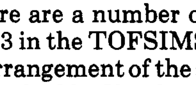
**Results and Discussion.** It can be clearly seen from both the positive (Figure 1) and negative (Figure 2) TOFSIMS spectra that the deuteration reaction used to prepare this polymer was successful and that no deuterium/hydrogen exchange reactions had occurred. This was particularly important to determine for our future investigations of these materials, as the synthetic scheme utilized Lewis acid chemistry ($AlCl_3$ with HCl in $C_6H_6$) to prepare the dichlorosilane as shown above. In terms of the fragmentation pattern of the deuterated PDMS (see Tables 1 and 2), three homologous series can quite readily be identified:

$^+[Si(CD_3)_2O]_nSi(CD_3)_3$ $n$ = 0, 1, 2, ... $m/z$ = 82, 162, 242, ...

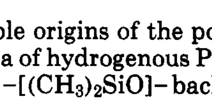
$^+[Si(CD_3)_2O]_nSi(CD_2)D$ $n$ = 0, 1, 2, ... $m/z$ = 46, 126, 206, ...

$\underline{[OSi(CD_3)_2]_nOSi(CD_3)_2OSi^+(CD_3)}$ rings $n$ = 0, 1, 2, ... $m/z$ = 142, 222, 302, ...

The deuteration does quickly allow one anomaly from the PDMS SIMS literature to be clarified and that is the hydrogenous PDMS peak at $m/z$ of 133 has been assigned to $^+Si_2OC_4H_{13}$ in the *Handbook of Static SIMS Spectra of Polymers*;[10] however, this would lead to $^+Si_2OC_4D_{13}$ ($m/z$ of 146) for deuterated PDMS. The assignment proposed here is to the homologous ring series shown above, where $m/z$ of 133 ($Si_2O_2C_3H_9$) or 142 ($Si_2O_2C_3D_9$) is clearly the cyclic dimer **I** or **II**, respectively.



I



II

This assignment is consistent with the results of Briggs for hydrogenous PDMS.[3,11]

There are a number of possible origins of the positive peak 73 in the TOFSIMS spectra of hydrogenous PDMS: (i) rearrangement of the skeletal $-[(CH_3)_2SiO]-$ backbone as described by Vanden Heuvel[12,13] with a methyl shift to

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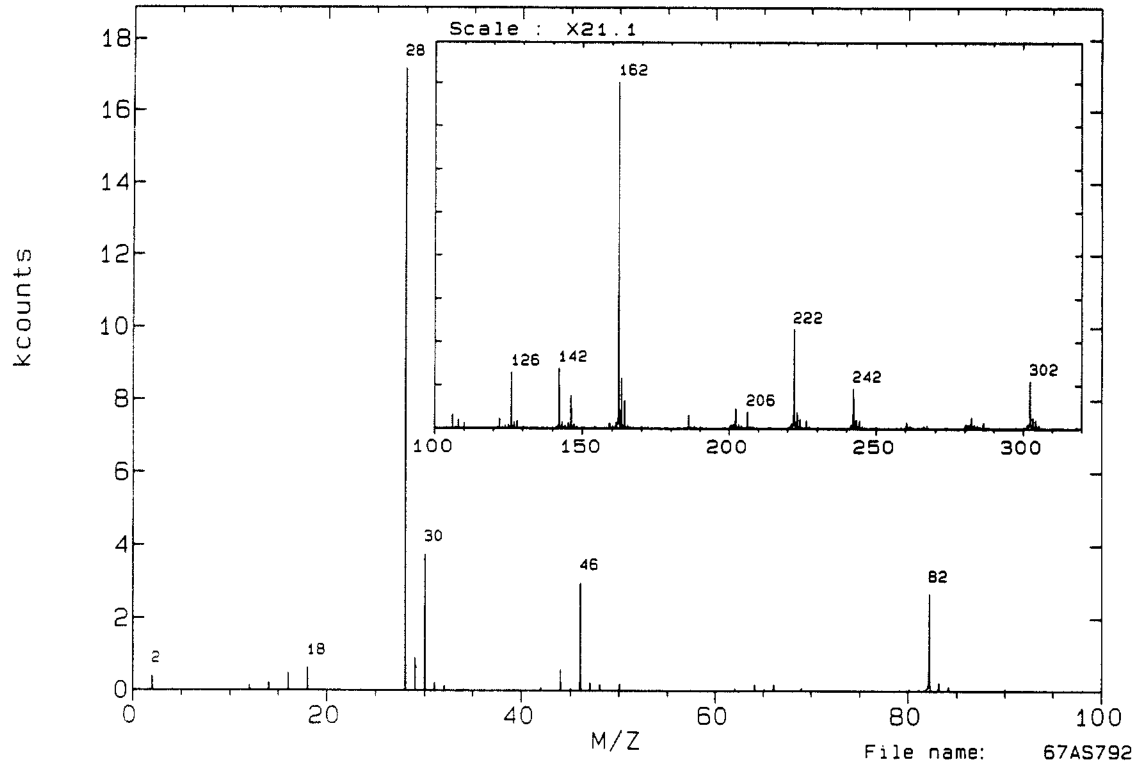

**Figure 1.** Positive TOFSIMS of deuterated PDMS $-[(CD_3)_2SiO]_n-$.

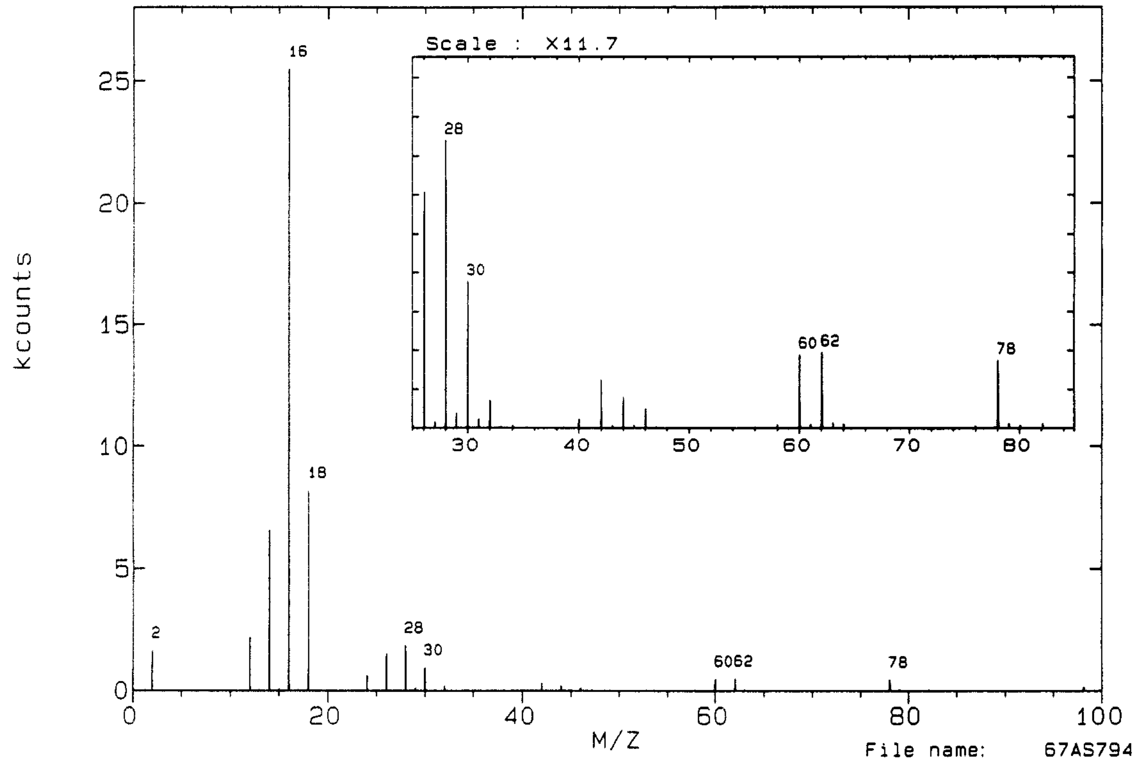

**Figure 2.** Negative TOFSIMS of deuterated PDMS $-[(CD_3)_2SiO]_n-$.

give $-Si(CH_3)_3$; (ii) migration of small amounts of trimethylsilyl-terminated PDMS $(CH_3)_3SiO[(CH_3)_2SiO]_nSi(CH_3)_3$ contaminant to the surface. As TOFSIMS is sensitive to just the first monolayer or two for small molecules or the first few angstroms for polymers (<5 Å), only trace amounts of the trimethylsilyl-terminated siloxane are needed to see this effect; (iii) orientation of the end groups of the polymer to the surface due to the lower surface free energy of the $-OSi(CH_3)_3$ unit relative to the $-[(CH_3)_2SiO]-$ skeleton. End groups also have entropic reasons to be at the surface of a polymer, although this effect is expected to be smaller than the surface energy effect from different terminal group chemistry. Again, the high surface sensitivity of TOFSIMS allows for the observation of this behavior, which would not be detected by other surface analysis methods such as XPS, due to their higher sampling depth into the polymer film; (iv) Hercules and co-workers[4] have suggested a fragmentation series (73, 147, 221, etc.) based on $CH_2Si(CH_3)O[Si(CH_3)_2O]_n^+$ for linear PDMS.

What then does the fully deuterated $-[(CD_3)_2SiO]_n-$ TOFSIMS give to help clarify these arguments? First,

**Table 1. Positive TOFSIMS Assignments for Deuterated PDMS $-[(CD_3)_2SiO]_n-$**

| *m/z* | composition | species |
|---|---|---|
| 2 | D | D |
| 18 | $CD_3$ | $CD_3$ |
| 28 | Si | Si |
| 30 | SiD | SiD |
| 46 | SiOD or $SiCD_3$ | SiOD or $Si(CD_2)D$ |
| 82 | $SiC_3D_9$ | $Si(CD_3)_3$ |
| 126 | $Si_2OC_3D_9$ | $Si(CD_3)_2OSi(CD_2)D$ |
| 142 | $Si_2O_2C_3D_9$ | $OSi(CD_3)_2OSi(CD_3)$ ring |
| 162 | $Si_2OC_5D_{15}$ | $Si(CD_3)_2OSi(CD_3)_3$ |
| 206 | $Si_3O_2C_5D_{15}$ | $Si(CD_3)_2OSi(CD_3)_2OSi(CD_2)D$ |
| 222 | $Si_3O_3C_5D_{15}$ | $OSi(CD_3)_2OSi(CD_3)_2OSi(CD_3)$ ring |
| 242 | $Si_3O_2C_7D_{21}$ | $Si(CD_3)_2OSi(CD_3)_2OSi(CD_3)_3$ |
| 302 | $Si_4O_4C_7D_{21}$ | $OSi(CD_3)_2OSi(CD_3)_2OSi(CD_3)_2OSi(CD_3)$ ring |

**Table 2. Negative TOFSIMS Assignments for Deuterated PDMS $-[(CD_3)_2SiO]_n-$**

| *m/z* | composition | species | *m/z* | composition | species |
|---|---|---|---|---|---|
| 2 | D | D | 30 | SiD | SiD |
| 16 | O | O | 60 | $SiO_2$ | $SiO_2$ |
| 18 | $CD_3$ | $CD_3$ | 62 | $OSiCD_3$ | $OSiCD_3$ |
| 28 | Si | Si | 78 | $O_2SiCD_3$ | $O_2SiCD_3$ |

one criticism of any laboratory that carries out siloxane polymerization reactions is that trimethylsilyl-terminated PDMS $(CH_3)_3SiO[(CH_3)_2SiO]_nSi(CH_3)_3$ contaminant is omnipresent! Clearly we see no evidence for the presence of protonated PDMS in our spectra despite the exposure of our deuterated PDMS sample to all our typical polymerization methodology—vacuum lines, solvents, glassware, rotary evaporators, vacuum ovens, etc., and even the workup for acquiring the TOFSIMS spectra. We are therefore quite pleased to be able to eliminate option ii in the case of our own experiments. When considering proposal iv, the homologous fragmentation series proposed by Hercules and co-workers[4] would give a positive peak at $m/z = 78$ for our corresponding deuterated homologous series $CD_2Si(CD_3)O[Si(CD_3)_2O]_n^+$. Thus by our deuteration of PDMS we can comfortably eliminate this assignment based on the positive SIMS spectrum where we see a positive peak at $m/z = 82$ (see Figure 1 and the assignments discussed above).

Our results are consistent with the origin of the positive peak $m/z = 73$ (or 82 in our fully deuterated polymer) of the TOFSIMS spectra being due to a rearrangement of the skeletal $-[(CD_3)_2SiO]-$ backbone of the hydroxyl-terminated deuterated siloxane $HO[(CD_3)_2SiO]_nH$, with a methyl shift to give $-Si(CD_3)_3$ (proposal i above). One other very unlikely possibility is that, despite our careful chemistry to give hydroxyl-terminated siloxane $HO[(CD_3)_2SiO]_nH$, very small amounts of monofunctional siloxane could terminate the chains as $(CD_3)_3SiO[(CD_3)_2SiO]_nSi(CD_3)_3$. This is rather difficult to believe, but were it true, then the preferred orientation of the end groups of the polymer to the surface due to the lower surface free energy of the $-OSi(CD_3)_3$ end groups relative to the $-[(CD_3)_2SiO]-$ skeleton would also account for the observed spectra. We are in the process of trying to eliminate this last possibility by changing the end-group chemistry by using different termination reactions.

Further studies of TOFSIMS of a variety of siloxane homopolymers and siloxane–organic block copolymers are in progress. The deuterated siloxanes are currently being studied as isotopic blends $-[(CD_3)_2SiO]_n-/-[(CH_3)_2SiO]_n-$ using small-angle neutron scattering.

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